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CO₂ Diffusion and Solubility in a Polystyrene-Polybutadiene Block
Copolymer with Highly Oriented Lamellar Morphology

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ABSTRACT

Solubility and diffusion coefficients for CO₂ in polystyrene/polybutadiene (SB) block copolymer films were measured in a pressure decay sorption apparatus at 1 atm over a temperature range of 20 to 90 °C. The morphology of the block copolymer specimens consisted of alternating S and B lamellae of approximately 100 Å thickness with excellent long range orientation perpendicular to the surface of the 0.02 to 0.05 cm thick films. Diffusion behavior in the copolymer was simulated using homopolybutadiene and homopolystyrene data along with a finite difference model based on the well-ordered morphology. Comparisons of the model predictions with the measured values of the effective diffusion coefficient for CO₂ in the copolymer revealed that the diffusion coefficient of CO₂ in the polybutadiene region of the copolymer was lower than in homopolybutadiene by a factor of 1.9 at 20 °C. This difference disappeared at the glass transition temperature of the polystyrene in SB. This temperature-dependent reduction of CO₂ diffusion in the polybutadiene regions of the block copolymer results from restrictions on chain motions of the polybutadiene blocks arising from their connection to the polystyrene blocks.

INTRODUCTION

Polymeric materials have gained importance in many transport applications including membranes in gas and liquid separations, and barriers in the packaging industries. Heterogeneous block copolymers provide the potential for creating new materials for these applications with mechanical and transport properties superior to those of the parent homopolymers [1]. Morphological features of microphase separated block

copolymers that can affect small molecule transport include the small size (ca. 10 nm) and narrow size distribution of domains, a high internal surface/volume ratio, and diffuse interfacial regions. Knowledge of the relationships between block copolymer morphology and the diffusion and permeation processes is essential for successful manufacturing and usage of these heterogeneous polymers.

Such structure/property relationships can be obtained by a combination of diffusion studies and detailed morphological investigation. In addition to providing transport parameters, diffusion studies can provide information about the internal structure and the chain behavior of heterogeneous polymer systems not accessible from conventional morphological characterization techniques such as transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS). Chain immobilization, relaxation kinetics and diffuse interfacial regions have been investigated in segmented polyurethanes and polybutadiene-polystyrene block copolymers using transport analyses [2-6]. Few studies exist, however, which have combined measurements of transport properties with detailed morphological information, and these have been complicated by domain structures with random macroscopic orientation.

This study involves the transient sorption of CO_2 into a polystyrene-polybutadiene block copolymer of well defined and highly oriented lamellar morphology. The sorption process was simulated using a model based on this simple geometry. Measurements of the transient sorption of CO_2 into the SB block copolymer and the corresponding S and B homopolymers allowed for the tests of the model predictions and for some insights regarding chain motions in the polybutadiene lamellae of the block copolymer.

EXPERIMENTAL SECTION

The CO₂ gas (Colony, Inc.) had a purity in excess of 99%. Polycarbonate (PC) and polyethylene terephthalate (PET), used for calibration of the sorption apparatus, were commercial products supplied by General Electric Co. and E. I. DuPont de Nemours & Co. under the trade names Lexan and Mylar (type A), respectively. The PC was supplied as a 0.025 cm thick sheet, and the PET as a 0.0125 cm thick sheet. Polystyrene (S) homopolymer was obtained from Polysciences , Inc., and polybutadiene (B ; 90% 1,4 addition) was obtained from Scientific Polymer Products, Inc; both homopolymers had molecular weights of 200,000 g/mole.

Phillips Petroleum Co. supplied a 0.05 cm extruded sheet of an experimental grade of polystyrene-polybutadiene block copolymer (SB) which was part of their K-Resin series. This block copolymer contained 75% (v/v) polystyrene and had a weight average molecular weight of 187,000 g/mol with $M_w/M_n = 1.5$ [7]. The steady - state permeation characteristics of this same material to Ne, Ar, Kr, N₂, CO₂, and CH₄ have been investigated by Csernica et al [7,8,24] , who also reported on the bulk morphology of the material; polybutadiene lamellae (ca. 100 Å thick) with excellent long-range orientation in the extrusion direction were observed via TEM and SAXS experiments. Specimens were prepared [7, 24] from this extruded sheet so that the lamellae were perpendicular to the surfaces of the disk-shaped films placed into the sorption apparatus .

Figure 1 is a schematic diagram of the apparatus used to measure transient sorption. Similar designs have been reported by a number of investigators [9-11]. The main components of the system include sample, storage and calibration volumes, a sensitive pressure transducer, and a data

acquisition system. The sample volume, A, is a 22.0 ml stainless steel Parr bomb fitted with a screw cap and two 0.20 mm thick lead gaskets to seal the cover to the bomb cup. The storage volume, B, and the calibration volume, C, are both Whitey stainless steel 40.0 ml cylinders. Volumes A and B are each connected to separate pressure transducers. An MKS Baratron type 590 high accuracy (0.09% of the reading) capacitance pressure transducer is connected to volume A; the temperature control and display unit for this transducer is an MKS 270b series signal conditioner. The transducer connected to volume B is an Omega model PX102 resistance pressure transducer with an accuracy of 1.0% up to 30 atm. The signal from the MKS transducer is collected by an Apple IIe computer through a Cole-Parmer model 8109-05 analog interface card. The A/D converter allowed a maximum sampling rate of 10 readings per second

Computation of the solubility coefficients required precise determination of the sample and the storage volumes. This was accomplished by measuring the gas expansion ratios [10] of volume A, volume B and volume C (a removable cylinder of known volume). The volume of the removable cylinder, V_c , was determined by filling it with several different liquids whose specific gravities were accurately measured with a pycnometer. When volume C was removed, a plug tightened to a predetermined etch mark was installed to prevent the introduction of unaccounted volume. The volumes of A (V_a) and B (V_b) were then calculated using the gas expansion ratios V_a/V_b and $V_a/(V_b+V_c)$, and the equation of state $PV=nZRT$ where Z is compressibility factor [23] and n is the number of moles of gas. Volumes calculated by this method agreed to within 0.4% for the four different expansion gases N_2 , Ar, CO_2 , and He.

Polymer films used in sorption experiments were disk shaped with a radius of 1.25 cm and a thickness of 0.02 - 0.05 cm. Two to ten disks were stacked in volume A between nickel screen spacers, and lead disk fillers were added to occupy most of the remaining volume (see Figure 1). To prevent leaks, new lead gaskets were used each time a new stack was inserted into the apparatus.

After the sample was loaded, a mechanical pump was used to evacuate volume A to about 10^{-2} torr, and the storage volume was filled with the test gas. The polymer was then degassed for at least twice the time required to reach sorption equilibrium. A sorption run was started by allowing a portion of the test gas into volume A from volume B and simultaneously starting the data acquisition program. The solubility and diffusion coefficients were measured at 1 atm over the temperature range 20 - 90 °C.

Diffusion Coefficient Analysis

A simple and standard model for sorption experiments was used to process the transient pressure decay data [12,13]. The experiment was modeled as one dimensional diffusion into a plane sheet with the penetrant entering perpendicular to the plane surfaces. The surface concentration was assumed to be independent of time since the pressure drop during the course of a sorption run was always less than 3% of the initial pressure. Edge effects were neglected since the ratio of disk thickness to radius was small (ca 0.03). A spatially uniform surface concentration was assumed since the screen spacers were of high porosity and offered negligible transport resistance; this assumption was verified when the same diffusion coefficient was measured for stacks of 2, 8, and 24 disks.

Crank presents several methods to obtain a diffusion coefficient from transient sorption data [12,13]. We employed two of these methods. The initial slope method takes advantage of the small time asymptotic limit of the sorption curve :

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{l^2 \pi} \right)^{0.5} \quad (1)$$

where M_t is the amount (g) of diffusant in the sheet at time t (sec), M_∞ is the amount of diffusant in the sheet at equilibrium, D is the diffusion coefficient (cm^2/sec), and l is the sheet thickness (cm). The diffusion coefficient is obtained from the slope of the linear portion of a plot of M_t / M_∞ vs $t^{0.5}$. The second method [12,13] uses the half-time ($t_{1/2}$ is the time required to sorb $M_\infty/2$) of the sorption process to calculate the diffusion coefficient.

$$D = \frac{0.05}{t_{1/2} / l^2} \quad (2)$$

Figure 2 contains a sorption plot for PC at 35 C. Diffusion coefficients calculated by the initial slope and half-time methods from these plots for PC and PET are listed with literature values in Table 1. There is good agreement between the measured values and those obtained by other investigators [14, 15, 18].

Solubility Coefficient Analysis

Solubility coefficient, S , was obtained from the volume of the penetrant absorbed at equilibrium (V_g), the volume of the polymer sample (V_p), and the final penetrant pressure (P_{eq})

$$S = \frac{V_g(\text{STP})}{V_p P_{eq}} \quad (3)$$

where STP indicates standard conditions of 273 K and 1 atm. The volume of the gas absorbed in the polymer was calculated from the number of moles of gas absorbed:

$$V_g(\text{STP}) = \frac{22.4 * (P_{in} - P_{eq}) * V_a}{R * T} \quad (4)$$

The final pressure (P_{eq}) was determined from the pressure transducer reading at sorption equilibrium, and the initial pressure reading (P_{in}) was estimated from an extrapolation of the pressure decay readings. Extrapolation was necessary because the temperature of the gas in volume A was as much as 10 °C higher than the surrounding bath at the start of a run; this temperature difference was caused by the compression of gas into volume A as it expanded from volume B. Approximately 1.2 minutes were required for the gas temperature to equilibrate with the bath temperature. Thus, the pressure decrease during the first minute of a sorption run included contributions from diffusion of gas into the polymer wafers and from thermal transients in the gas. Therefore, the initial pressure was calculated by extrapolating to zero time the straight line portion of the pressure decay plot starting at times greater than 1 minute. As seen in Table 1, there is good agreement between the solubility coefficients calculated for PC and PET from our sorption experiments and those obtained from various literature sources [16, 17].

RESULTS AND DISCUSSION

Solubility coefficients

Figure 3 summarizes the temperature dependence of the equilibrium solubility coefficients for CO₂ in B, S, and SB. The heats of solution (kJ/mole) calculated from these plots by a least squares method were -9, -22, and -15 for B, S, and SB, respectively. It is of interest to compare the observed block copolymer solubility to that predicted from homopolymer values. The solubility coefficient is an equilibrium property which can be described for a heterogeneous polymer system as a linear combination of the homopolymer values [19]

$$S^* = v_S S_S + v_B S_B \quad (5)$$

where S_S and S_B are the solubility coefficients for the pure materials, S^* is the solubility coefficient for the composite, and v_S and v_B are the volume fractions in the composite.

The expectation of agreement between the calculated S^* and the observed values of S_{SB} for the block copolymer relies on the assumption that solubility coefficients of the homopolymers adequately describe the solubilities of the polystyrene and polybutadiene moieties of the block copolymer. The glass transition temperatures (T_g) of the polystyrene and polybutadiene domains of the block copolymer were determined by DSC at a heating rate of 20 °C/min. The polystyrene moiety of the SB diblock had a T_g of 367 K; T_g of the polystyrene homopolymer was 373 K. Toi and Paul [20] have determined that CO₂ solubility decreases as the T_g of a polystyrene sample decreases. The polystyrene homopolymer solubility value, S_S , used in equation (5) was adjusted to account for this dependence of solubility on glass transition temperature.

Table II compares the values of S^* from equation (5) with those obtained from the sorption experiments (S_{SB}). There is good agreement between the calculated and observed values. Thus, the simple two phase

model given by equation (5) adequately describes the equilibrium properties of the block copolymer, i.e. the solubility coefficients, over a range of temperatures.

Diffusion coefficients

The CO₂ diffusion coefficients for B, S, and SB were plotted as a function of temperature in an Arrhenius form in Figure 4. The apparent activation energy for diffusion, E^D (kJ/mole), calculated from these plots by a least squares analysis were 19, 28, and 32 for B, S and SB respectively. Although the diffusion coefficients for the SB diblock lie between those of the S and B homopolymers, the apparent activation energy for SB is larger than for either of the homopolymers. This surprisingly large temperature dependence of the block copolymer diffusion coefficient was investigated by simulating the measured SB diffusion coefficient based on the behavior of the component homopolymers.

We recall that the analysis used to calculate the D from the transient experiment was formulated for sorption into homogeneous materials and is equal to the steady-state D . The steady-state D for a composite material of sheets in parallel, such as the K-Resin, has been described as a linear combination of the component steady-state diffusion coefficients weighted by their respective volume fractions [13]. Because the K-Resin is a composite, the effective diffusion coefficient, D_{eff} , calculated from equations (2) or (3) is not necessarily equal to the steady-state diffusion coefficient of the material. The D_{eff} calculated for SB from the transient sorption experiment can not be obtained from a linear combination of the homopolymer diffusion coefficients.

In order to relate the measured K-Resin diffusion coefficient, D_{eff} , to homopolymer values, a computer model was developed to simulate the non

steady-state diffusion into a composite medium of well defined structure. The spatial discretization used to describe the composite appears in Figure 5. The following assumptions have been employed: (i) continuous lamellae connect the film surfaces, (ii) two dimensional diffusion takes place in the x-y plane, (iii) diffusion coefficients are independent of concentration, (iv) the diffusion is Fickian [13], (v) surface concentrations are independent of time and position, (vi) the interfaces between the lamellae are sharp, (vii) gas concentrations, c , in the microphase regions are $c_S = K \cdot c_B$ where K is a partition coefficient equal to the ratio of solubility coefficients, S_S/S_B . The equations to be solved are:

$$\partial c_S / \partial t = D_S (\partial^2 c_S / \partial x^2 + \partial^2 c_S / \partial y^2) \quad (6)$$

$$\partial c_B / \partial t = D_B (\partial^2 c_B / \partial x^2 + \partial^2 c_B / \partial y^2) \quad (7)$$

where S and B denote the continuous lamellae; equations (6) and (7) are subject to boundary conditions

i) $c_S = c_B = 0$	$t = 0$
ii) $c_S(y=y_0, t) = c_B(y=y_0, t) = C_0$	$t > 0$
iii) $\partial c_B / \partial x = 0$	$x = x_0, \text{ all } t$
iv) $\partial c_S / \partial x = 0$	$x = x_{nx}, \text{ all } t$
v) $\partial c_S / \partial y = \partial c_B / \partial y = 0$	$y = y_{ny}, \text{ all } t$
vi) $D_S \partial c_S / \partial x = D_B \partial c_B / \partial x$	$x = x_i, \text{ all } t$

A forward finite difference method [13] was employed to solve the equations (6) and (7) using the measured homopolymer values for D and S from 20 to 90 °C as input.

The transient sorption curves generated by the model (see Figure 6 for an example) were analyzed with the half-time method to yield an effective diffusion coefficient, D_{eff} , which increased with the ratio of thickness to width (n_y / n_x) used in the the model, and approached a limiting value at large n_y / n_x . Since the actual n_y / n_x of the K-Resin film was around 25,000 [film thickness = 0.5 mm, lamellar thickness $\approx 200 \text{ \AA}$] large amounts of computer time would have been needed for an exact calculation of D_{eff} . Instead, the limit was approximated by constructing a plot of D_{eff} vs $(n_y/n_x)^{-1}$ and extrapolating the resulting linear plot to $(n_y/n_x)^{-1} = 0$ to obtain the desired asymptotic value of D_{eff} .

Figure 7 is an Arrhenius plot which compares D_{eff} values calculated from half times of the model and the experimental sorption curves. The model overpredicts the measured Kresin diffusion coefficients at the lowest temperature of 293 K by a factor of about two; deviations between model predictions and experimental values decrease as the test temperature approaches T_g of polystyrene. Because the finite difference model uses homopolymer data as input, the observed discrepancy suggests an additional impedance to gas diffusion in the block copolymer not found in the homopolymers. We will suggest below that this extra resistance to gas flow and its temperature dependence are the causes of the unusually high apparent activation energy for diffusion in the K-Resin which was noted earlier (Figure 4).

A similar phenomenon was observed in the Kresin permeabilities [7,24] which were measured using CO_2 in a variable-volume steady state permeation apparatus. Activation energies for permeation obtained from Arrhenius plots of permeability coefficients in the temperature range 25 - 50 °C for the block copolymer (EP_{SB}) and the homopolymers (EP_S , EP_B) are

19.7, 11.7, and 8.4 kJ/mole, respectively; E^P of the K-Resin is significantly larger than either homopolymer value. Although a 3 - component model which includes an interfacial zone more completely describes the K-Resin (7), for simplicity here the steady state permeability coefficient will be approximated using a two component parallel model [19]:

$$P_{\text{par}} = v_B P_B + v_S P_S \quad (8a)$$

where P_S , P_B , and P_{par} are the permeability coefficients for polystyrene, polybutadiene, and the parallel composite, respectively. P_S and P_B can be expanded into Arrhenius expressions to consider temperature dependence [21]:

$$P_{\text{par}} = v_B P_{o,B} \exp(-E^P_{B}/RT) + v_S P_{o,S} \exp(-E^P_{S}/RT) \quad (8b)$$

The apparent activation energy for the parallel system (E_{par}), i.e. that derived from the slope of an Arrhenius plot, can be obtained from the local derivative $\partial(\ln P_{\text{par}})/\partial(1/T)$.

$$E^P_{\text{par}} = E^P_B (v_B P_B / (v_B P_B + v_S P_S)) + E^P_S (v_S P_S / (v_B P_B + v_S P_S)) \quad (9)$$

Equation (9) states that the apparent activation energy for permeation is an average of the homopolymer activation energies weighted by respective fractions of the total flux. Because the polybutadiene is considerably more permeable to CO_2 than polystyrene [7,8], E^P_{par} for this system is dominated by E^P_B and the activation energy for the K-Resin is expected to be close to that for polybutadiene. Using equation (9), the calculated E^P_{par} is 8.8 kJ/mole, which is close to that of homopolybutadiene (8.4 kJ/mole) as expected but significantly lower than the experimental value of E^P_{SB} (19.7 kJ/mole). This observation is consistent with the information from the diffusion studies.

As indicated by the comparison between the measured and simulated diffusion coefficients, CO_2 transport through the copolymer is hindered

relative to that predicted from the homopolymer components. A number of workers have attributed similar observations of gas impedance in block copolymers to the influence of the diffuse interfacial region between domains [3,5,6,7]. Small angle neutron scattering and gas permeation experiments have determined the interfacial region in SB to be about 25 Å [7].

The interfacial region was considered to determine whether its presence was sufficient to explain the disagreement between the measured and calculated D_{eff} of the K-Resin. The interfacial region can be treated as a random copolymer varying spatially in composition between boundaries from pure styrene to pure butadiene [7]; the average diffusion coefficient of the interface is bracketed by the homopolystyrene and homopolybutadiene values. As a first consideration, the interfacial diffusion coefficient was assumed equal that for S, thereby maximizing its influence in impeding transport. This analysis effectively creates a new heterogeneous copolymer of 12.5 % B and 87.5 % S. For this limiting case the value of D_{eff} at 293 K generated by the model was $56 \times 10^{-8} \text{ cm}^2/\text{sec}$, a value still significantly larger than the observed value of $44 \times 10^{-8} \text{ cm}^2/\text{sec}$. The diffuse interface therefore does not completely explain the discrepancy between the measured and calculated values of D_{eff} shown in Figure 7.

Interactions between the separate regions of heterogeneous materials have also been proposed to explain unexpected restrictions on gas transport in such materials [2,4,5]. For the case of SB block copolymers, the location of the covalent junction between the polystyrene and polybutadiene blocks in the interfacial zone between the lamellae may reduce chain mobility in the polybutadiene region beyond the interface, thereby decreasing the rate of gas diffusion through the rubbery block

analogous to the decrease of gas diffusion observed in polybutadiene crosslinked with electron beam irradiation [22,24]. In the SB block copolymer the restriction on chain mobility, and thus the unexpected retardation of gas diffusion, should disappear as the mobility of the polystyrene block increases, i.e. as the polystyrene glass transition temperature is approached.

In order to account for this chain immobilization of the B regions of the copolymer, we decreased the input values to the computer model for the gas diffusion coefficients of CO₂ in the polybutadiene. The extent of adjustment defined a temperature dependent factor

$$\beta = D/D^* \quad (10)$$

where D is the diffusion coefficient of CO₂ through homopolybutadiene, and D* is the adjusted input value to the model, i.e. the presumed diffusion coefficient of CO₂ through the B block of the SB block copolymer. β combines contributions to chain immobilization outside the interfacial zone and within the interfacial region into a single parameter which describes the restricted mobility of the entire polybutadiene block of the SB. Michaels and Parker [25] in a study of semicrystalline polyethylene attributed a similar immobilization factor to the crosslinking action of crystallites which restricted the chain mobility in the amorphous phases.

At each temperature, a value of β was chosen so that the prediction of our model matched the measured value of Deff. Table III lists β values at several temperatures which are in reasonable correspondence with the results of Odani et al [5] who calculated values of β for various gases at a single temperature using a styrene-butadiene block copolymer. The immobilization factors at 25 °C reported by Odani et al were 0.99, 1.3, 1.8, 2.4 and 2.4 for He, Ar, N₂, Kr, and Xe, respectively.

Chain immobilization of and restricted diffusion in the polybutadiene regions of the SB block copolymer is caused by the polystyrene regions and the magnitude of this effect depends on the mobility of the polystyrene. At the lowest temperature of our experiment, the polystyrene chains have the least motion, and immobilize the PB chains to the greatest extent (highest β). This immobilization is expected to decrease as temperature increases, and it should essentially disappear at the polystyrene T_g . This trend is observed in Table III; β approaches unity as the temperature approaches the T_g of the polystyrene block.

SUMMARY

The use of an SB block copolymer with well ordered lamellar microstructure facilitated the simulation of transient CO_2 sorption experiments using the pure component homopolymer behavior as input. Comparison of measured and model-calculated block copolymer diffusion coefficients revealed significant differences in gas transport through the polybutadiene regions of the block copolymer and the corresponding polybutadiene homopolymer. The polybutadiene of the block copolymer contained an additional temperature dependent resistance to gas transport (permeability or diffusion) not observed in the polybutadiene homopolymer. Restriction of chain motion caused by the chemical connection of the polybutadiene to the glassy polystyrene in the heterogeneous SB block copolymer underlies this observed extra resistance to gas transport. The equilibrium solubility of the CO_2 in the B regions of the SB diblock was not influenced by these restrictions on molecular motions; equilibrium solubilities of CO_2 in SB at various temperatures were

adequately described by a volume-fraction weighted combination of the homopolymer solubilities.

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Table 1

Measured and reported CO₂ transport coefficients

Transport parameter	PC (35 °C)	PET (35 °C)
D (cm ² /sec)		
initial slope	2.5 *10 ⁻⁸	1.3 *10 ⁻⁹
half time	2.3 *10 ⁻⁸	1.2 *10 ⁻⁹
literature	3.0 *10 ⁻⁸ [14]	1.5 *10 ⁻⁹ [15]
S (cc(STP))/(cc*cm Hg))		
measured	4.1 *10 ⁻²	1.3 *10 ⁻²
literature	4.6 *10 ⁻² [16]	1.4 *10 ⁻² [17]
Activation energy		
for diffusion Ed (Kcal/mole)		
measured	8.4	
literature	9.0 [18]	

Table 2

Comparison of measured and predicted CO₂ solubility in SB

Temperature [K]	Measured S_{SB}^a	Predicted $S^*(\text{eqn 5})$
293	2.0	2.3
303	1.6	1.8
323	1.0	1.1
363	0.6	0.6

^a units on solubility: $10^{-2} \cdot \text{cm}^3(\text{STP})/\text{cm}^3(\text{polymer})/\text{cm Hg}$

Table 3

CO₂ immobilization factor in SB

Temperature [K]	D * 10 ⁷ [cm ² /sec]		
	B	B*	β
293	32	16	1.9
323	75	50	1.5
343	104	80	1.3
363	150	136	1.1

Figure Legends

Figure 1. Schematic of dual-volume apparatus used in pressure decay sorption studies.

Figure 2. Measured sorption curve for CO₂ uptake into a PC sheet.

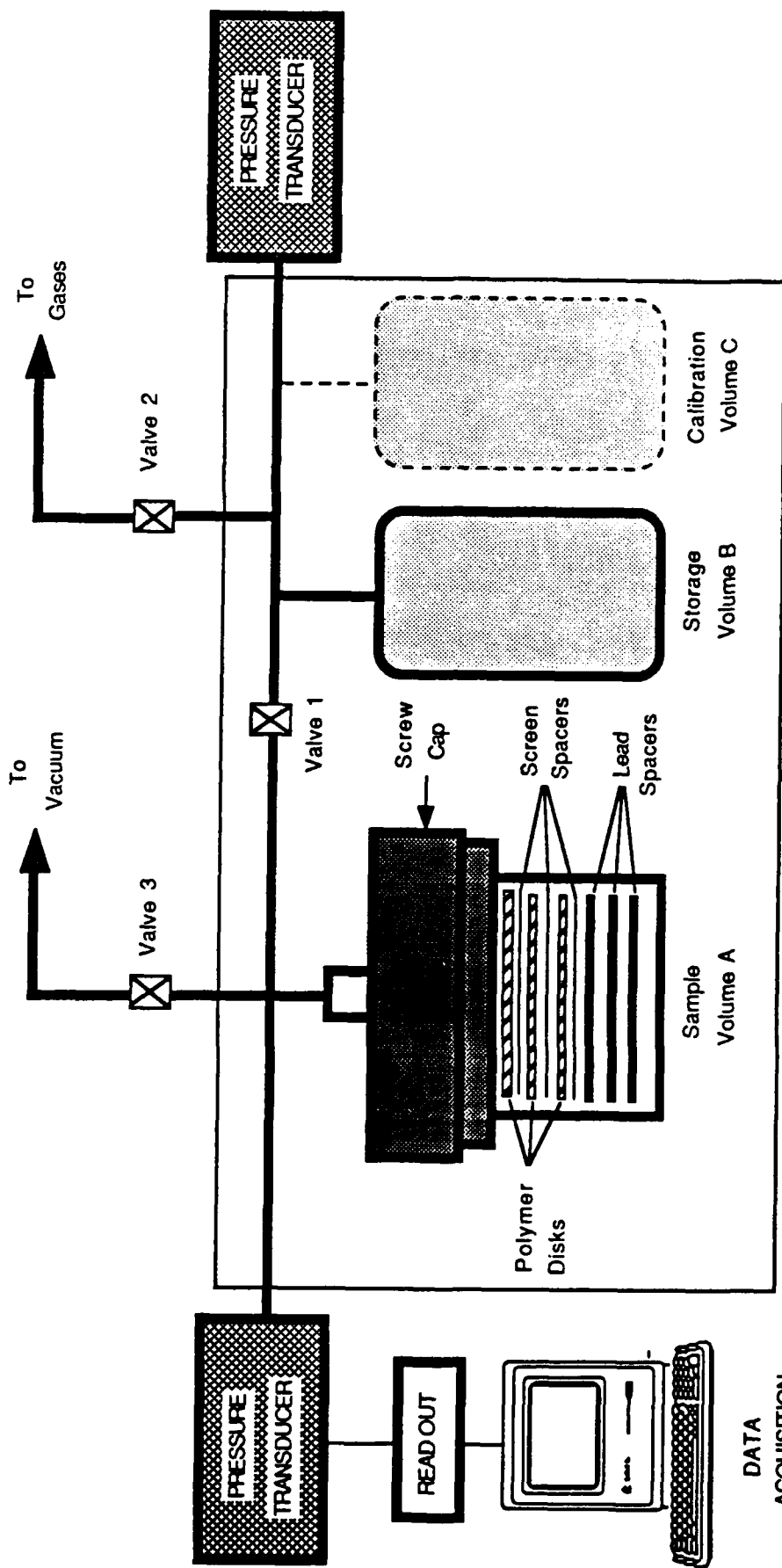
Figure 3. Temperature dependence of the equilibrium CO₂ solubility coefficients for S, B, SB.

Figure 4. Arrhenius plots of the diffusion coefficients for CO₂ in S, B, SB.

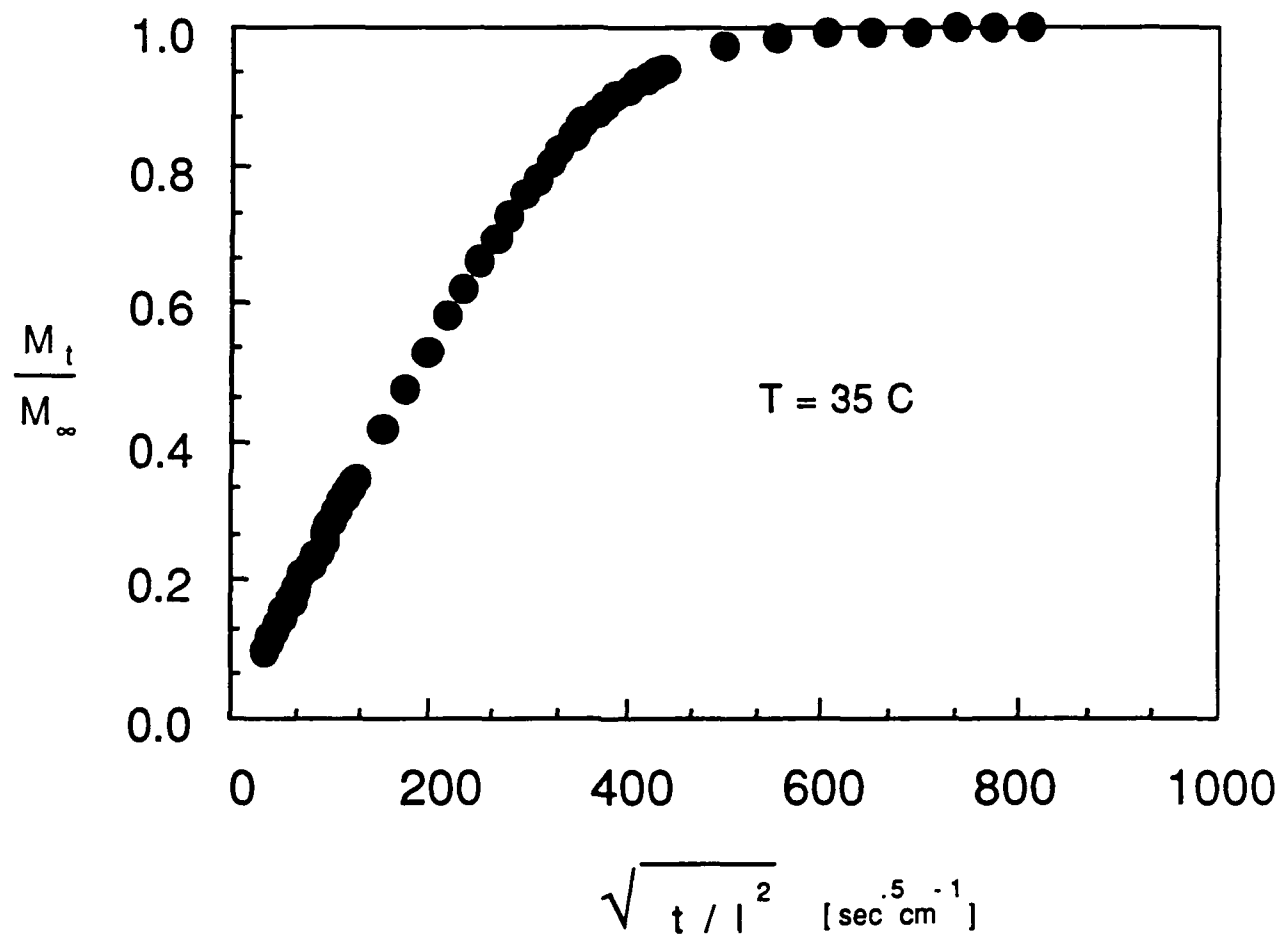
Figure 5. Spatial discretization of SB used in finite difference model to simulate sorption behavior.

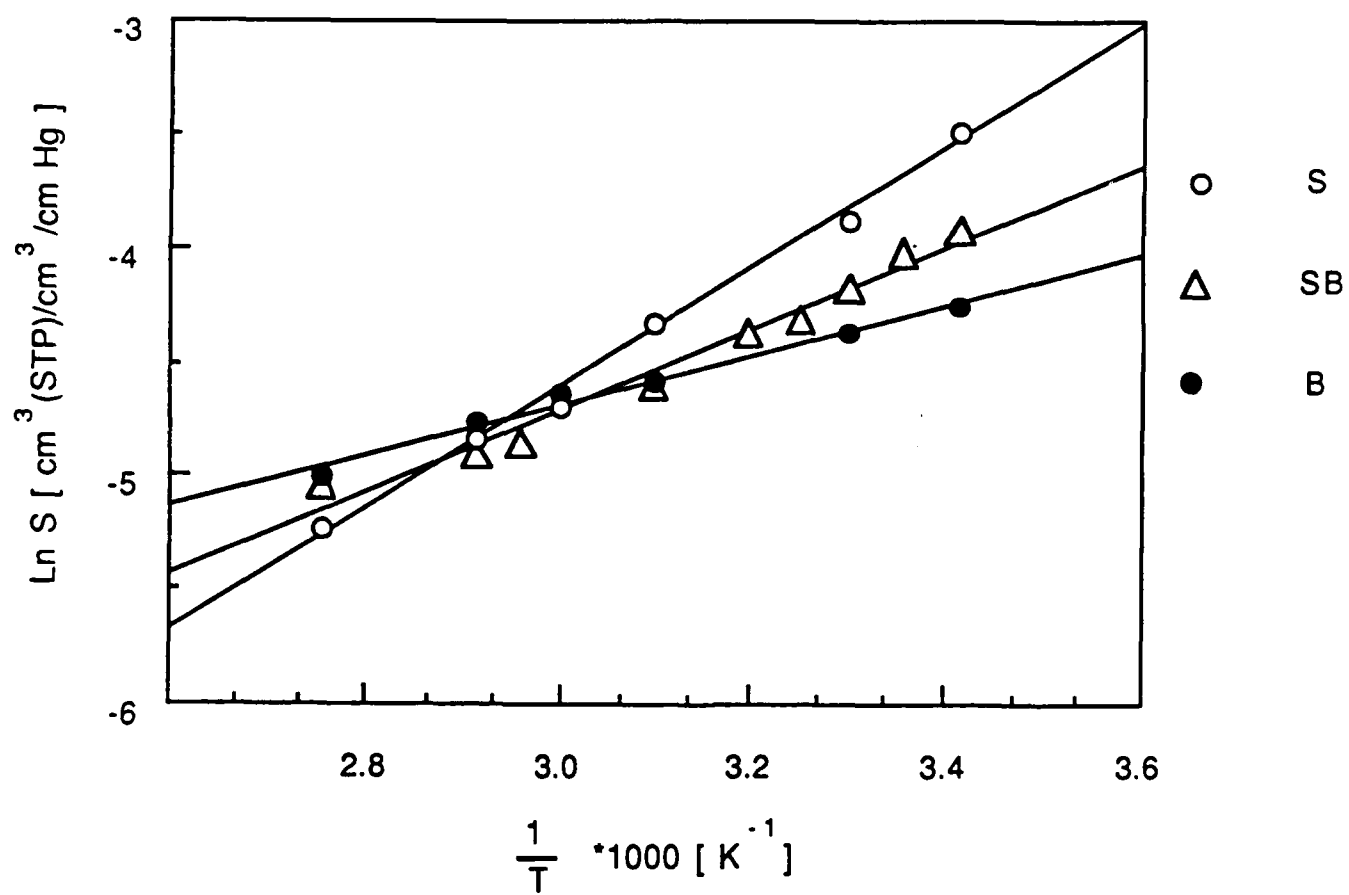
Figure 6. Comparison of measured CO₂ uptake in SB at 293 K with calculated sorption curves based on the model in the text using n_y/n_x values of 1.4, 3 and 9. The De_{eff} calculated for $n_y/n_x = 9$ is 75% of the asymptotic limit for De_{eff} at infinite n_y/n_x . Although the shapes of these sorption curves are similar to those exhibited by homopolymers, volume fraction weighted linear combinations of diffusion coefficients fail to predict the De_{eff} values generated either by the model or from the sorption data.

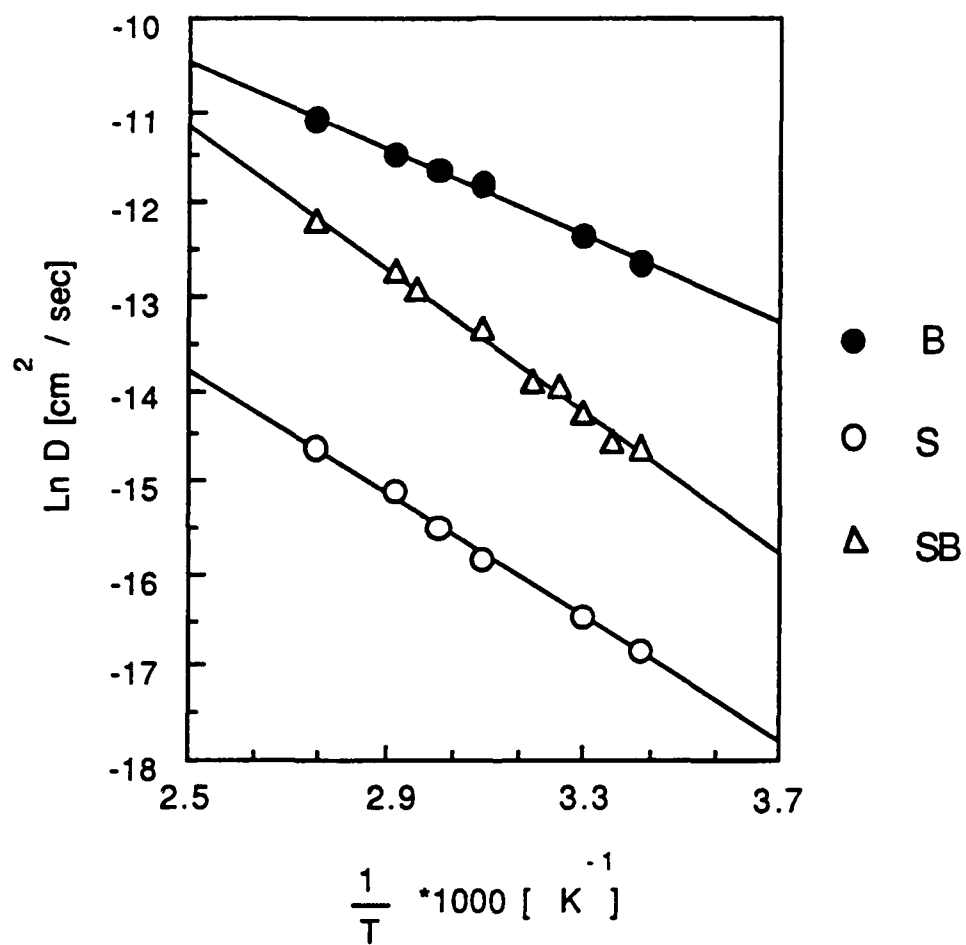
Figure 7. Comparison of Arrhenius plots for measured and model-generated CO₂ diffusion coefficients.

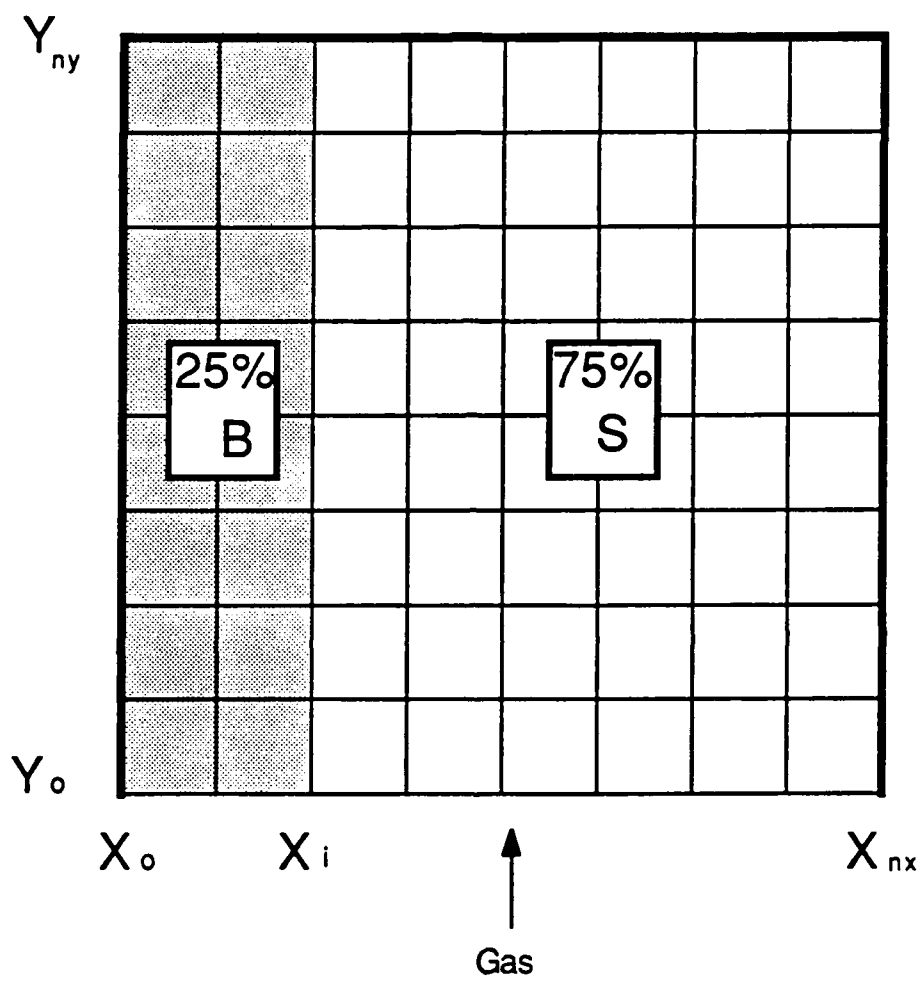


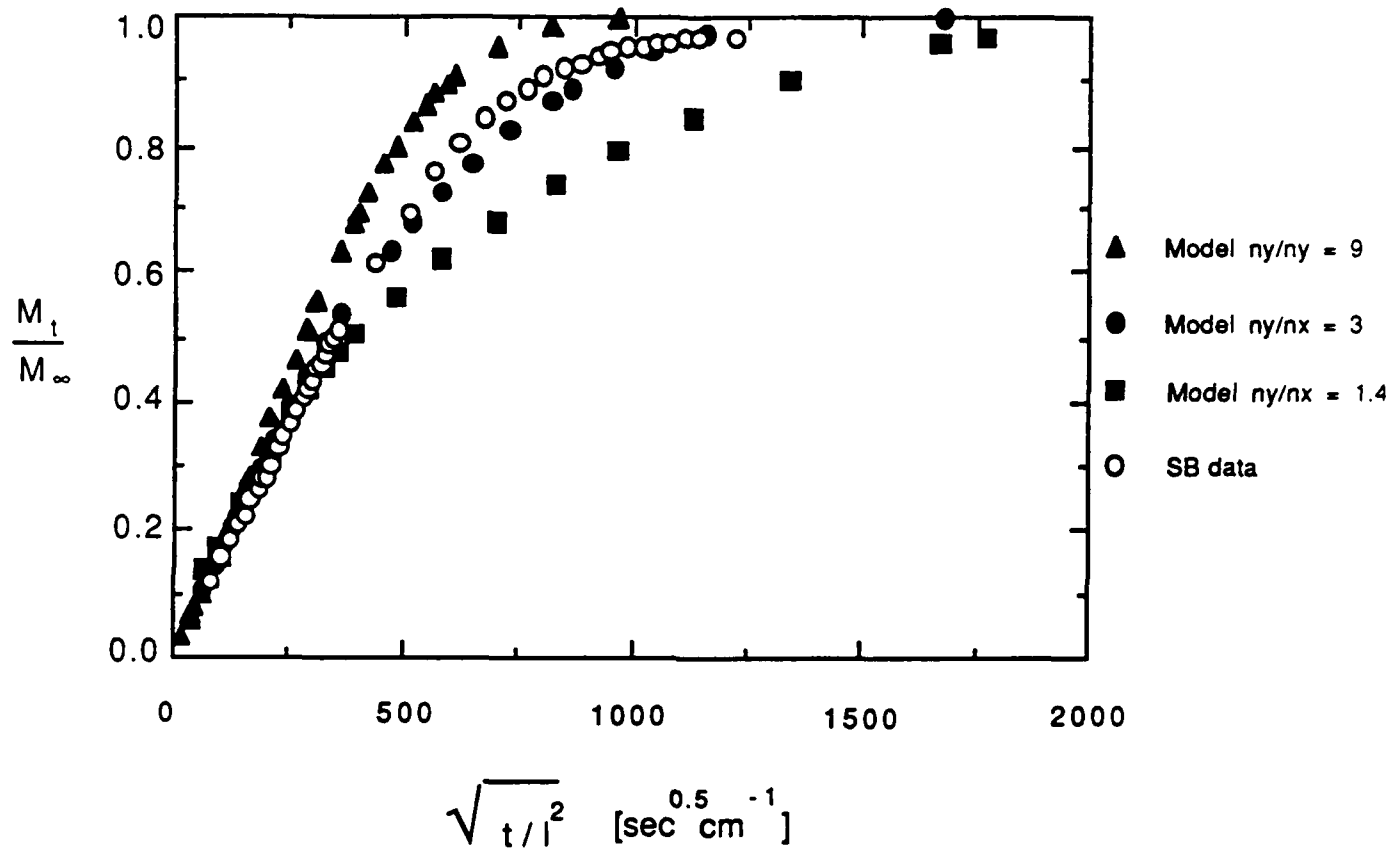
Constant Temperature Bath

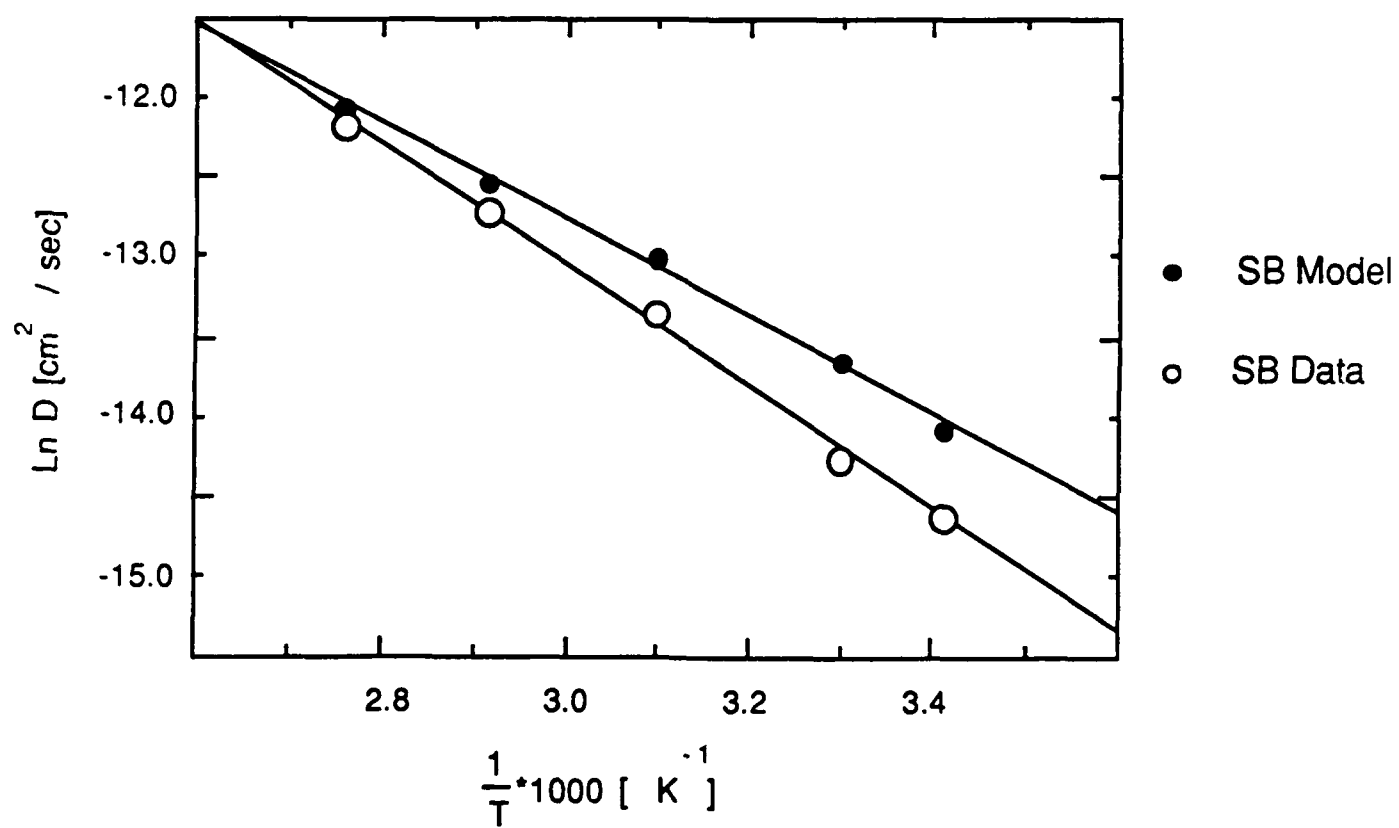












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